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Metastable zone width, Growth, Structural, Thermal, Spectral and SHG studies of Triglycine Sulpho Salicylate (TGSS) single crystals

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Abstract : Triglycinesulphate crystal is a well known ferroelectric crystal. In this work TGS salt mixed with salicylic acid to prepare TGSS salt .Solubility, metastable zone width and induction period for TGSS salt were measured at different supersaturation ratios. The critical nucleation parameters were evaluated based on the classical theory of homogeneous nucleation. Using the optimized nucleation parameters, single crystals of TGSS salt were grown by slow evaporation technique. Structural, spectral, thermal and SHG studies were carried out for the grown crystals and the results are discussed.
Key words : TGS; Nucleation; bulk crystal; growth from solutions; XRD;FTIR; supersaturation; TG/DTA; SHG.

1. Introduction

Triglycine Sulfate (TGS) crystal is a useful ferroelectric material founded in 1956 and has low dielectric constant and large pyroelectric coefficient. It finds applications in the fabrication of pyroelectric Videocon tubes, capacitors, transducers, sensors and also it is used in the infrared detection techniques as commercial products [1]. TGS crystal is monoclinic below and above Curie temperature (49 ^{o}C). The space group transforms from P21 in the ferroelectric phase to centrosymmetrical P21/m in the paraelectric phase [2-4]. It is observed that undoped TGS crystals have some disadvantages crystals such as high mobility of ferroelectric domains at room temperature, easy depolarization by electrical, mechanical and thermal means, microbial contamination with time during the growth and low Curie point etc [5-10]. Many organic and inorganic dopants have been used by researchers in order to overcome these disadvantages and in this work add salicylic acid in different molar ratios into TGS sample to prepare Triglycinesulpho-salicylate (TGSS). The ferroelectric transition temperature of TGSS crystal is to be at 52^{o}C. It is known that growth kinetics, morphology and quality of TGS crystals have been altered when salicylic acid is used as the admixture material. Considerable interest has been stressed on TGS material because it is a near room temperature ferroelectric and is a technologically important material. In this work, TGS salt mixed with salicylic acid to form Triglycinesulphosalicylicate (TGSS) crystal and the studies on nucleation kinetics, structural, spectral ,thermal, and SHG studies of the grown crystals are reported.

2. Nucleation and Relevant Equations

There are two steps to form a crystal from supersaturated solution and they are (i) formation of nucleus and (ii) the growth of this nucleus into a crystal. The first step gives an idea of thermodynamic of nucleation and growth, whereas the second step deals with the kinetics of these processes. Crystallization starts with nucleation and control of nucleation is crucial for the control of the number,size ,perfection , polymorphism and other characteristics of crystalline materials. When few atoms , ions or molecules join together in a supersaturated solution is the Gibbs free energy change . Once the nucleation occurs in the supersaturated solution , the nucleus grows quickly and a bright sparkling particle is seen. The time interval in which the observation of the first sparkling particle in the undisturbed supersaturated solution is called the induction period(t). The expression for the induction period in terms of Gibb's free energy is given by ln t = -B+DG/ kT where B is a constant, k is the Boltzmann's constant and T is absolute temperature. The Gibbs free energy will be maximum for a certain value of radius (r*) of nucleus , which is known as critical radius . Supersaturation ratio S is given by $S= C/C_0$ where C is the supersaturated concentration and C_0 is the saturated concentration [11,12] The number of crystals produced in the supersaturated solution is expressed as nucleation rate(J) can be calculated using the equation J=A exp (-DG*/(kT)) where A is pre-exponential factor and it is given by A=v*ZN where v* is the frequency of attachment ($v^* \sim 300 s^{-1}$), Z is Zeldovich factor (z=0.01), N is the concentration of molecules ($n= 10^{18}\ cm^{-3}s^{-1}$) and approximately $A=1x10^{24}$ for solution [13,14].The derivationsfor equations of critical nucleation parameters such as r*, σ, ΔG* and n are given in the literature [15].

3. Experimental and Results

3.1 Synthesis, Metastable Zone Width and Growth

In the present study to synthesize 20 mole % of salicylic acid added TGS sample, glycine, sulphuric acid and salicylic acid were taken in 3: 0.8: 0.21 molar ratio. The reactants were dissolved in deionized water, stirred well, heated at 50 °C to get the 20 mole% of salicylic acid admixtured TGS salt. Solubility of the salicylic acid admixtured TGS samples with various temperatures was measured by gravimetrical method[16].

Metastable zone width (MSZW) is a basic and an important parameter in terms of temperature for growing a crystal by solution growth technique. In the present work , the meta stable zone width of TGSS was measured by means of the conventional poly thermal method [17].Saturated solution of TGSS has been prepared in accordance with the presently determined solubility data. The studies were carried out in a constant temperature bat controlled to an accuracy of ±0.01° C provided with a cryostat for cooling below room temperatures. A constant volume of 10 ml of solution was used in all experiments. The solution was preheated to 5°C above the saturated temperature for homogenization and left at the superheated temperature for I hr before cooling. The equilibrium saturated solution is cooled from the over visible crystal nucleus in the solution is cooled from the over heated temperature and the temperature at which the first visible crystal nucleus in the solution is noted and this is the nucleation temperature. This experiment was carried out for the solution saturated at 30, 35, 40,45,50,55, and 60°C. Repeated trails were performed to ascertain the correctness of the observed results. The solubility curve and nucleation curve for TGSS sample are given in the Figure 1.

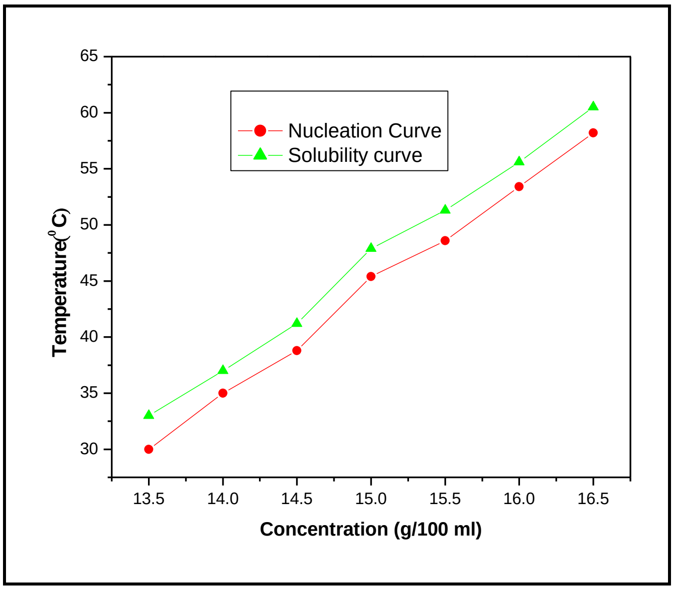

Figure .1: Metastable zone width of TGSS crystal

From the graph Figure 1, the solubility of TGSS sample in water increase with increase in temperature and hence the sample has positive temperature coefficient of solubility. The difference between the saturation temperature and nucleation temperature in the nucleation curve is called the metastable zone width. It is evident from the plots that the metastable zone width is slightly border in the higher temperature region whereas in the lower temperature region the width is tending to become narrow. For the maximum yield uncontrolled nucleation should be avoided and the growth of a crystal occurs from a solution maintained in the metastable condition.

3.2 Induction Period

Induction period was measured for supersaturated solution of the TGSS samples using water as the solvent at different values of supersaturation ratio and these values are used to determine critical nucleation parameters. Using the solubilitydata, the supersaturated solutions of salicylic acid added TGS salts were prepared at the selected supersaturation ratios viz. 1.3, 1.35, 1.4, 1.45 and 1.5. The induction period was measured for each supersaturation ratio by isothermal method. The variations of induction period with supersaturation ratio for the samples are presented in the figure.2. Using the values of induction period, the critical nucleation parameters were determined. From the figure..3, plots of $\ln\tau$ against $1/(\ln S)^2$ are approximately linear which explains the classical theory of homogeneous nucleation and the values of slope (m) were obtained. The calculated values of Gibbs' free energy change, radius of critical nucleus, number of molecules in the critical nucleus with the supersaturation ratio (S) and nucleation rate are tabulated in Table.1. Studies on nucleation kinetics of crystalline samples were carried out in order to have the controlled nucleation rate. The number of crystals produced in the supersaturated solution is expressed as nucleation rate i.e. the number of crystals produced per unit volume per unit time. The variables that affect the nucleation rate are pH, supersaturation, temperature and interfacial tension of the solution. Decrease in induction period and increase in interfacial tension are expected to increase the nucleation rate. With the optimized values of induction period, the growths of salicylic acid admixtured TGS crystals have been grown from aqueous solutions. Growth of salicylic acid admixtured TGS crystals was carried out by solution method with slow evaporation technique at room temperature (31^{o}C). Synthesized and re-crystallized salt of salicylic acid admixtured TGS are used to prepare the saturated solutions and the growth was carried out by slow evaporation technique. The optimized growth parameters from the studies of nucleation kinetics were used to grow good quality bulk single crystals. It took about 30 to 40 days to harvest the crystals. Grown crystalis shown in figure.4 and the grown crystals are found to be non-hygroscopic, transparent and colorless. It is to be mentioned here that when TGS crystals are added with salicylic acid, the transparency is less.

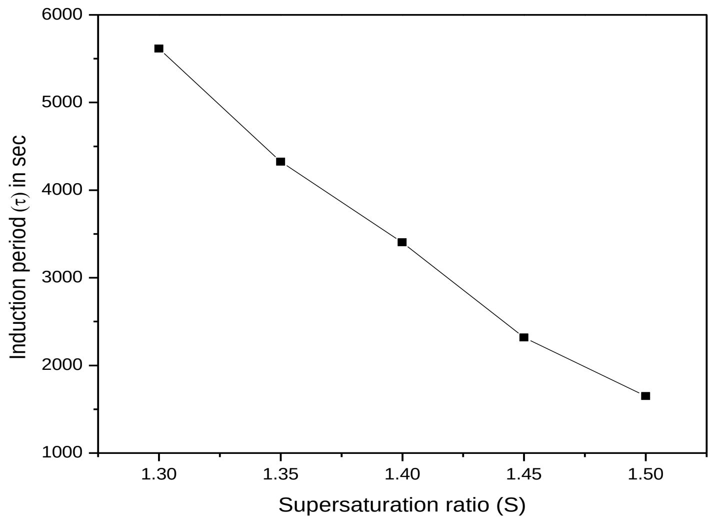

Figure .2: Variation of induction period (τ) with supersaturation ratio (S) for solution of TGSS sample.

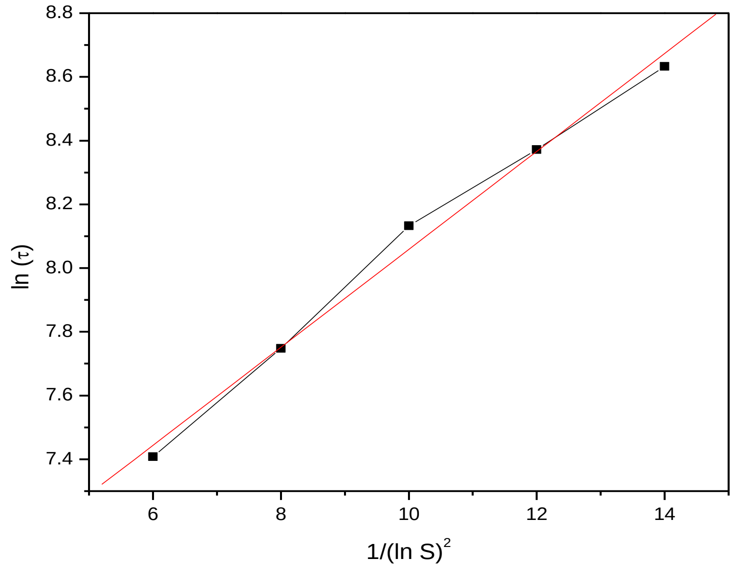

Figure.3 The plot of $1/(\ln S)^2$ versus ln τ for solutions of TGSSsample

Table .1 : Summary of critical nucleation parameters for TGSS sample

Sample	S	τ (sec)	ΔG* (10^{-21}) (J)	r* (10^{-9}) m	n	σ (10^{-3}) J/m^2	J x10^{24} (Nuclei/Sec/Volume
TGSS	1.3 1.35 1.4 1.45 1.5	5615 4324 3404 2317 1649	11.145 10.045 6.945 5.9652 4.784	1.214 1.124 0.9412 0.8419 0.7412	19 13 11 8 6	2.0669	0.312 0.6413 1.147 1.9412 2.387

Figure .4 : Grown crystal of TGSS sample

3.3 Structural Analysis

The grown salicylic acid admixture TGS (TGSS) crystals are characterized structurally by single crystal XRD studies. The obtained data from single crystal XRD studies are given in the Table .2. From the data, it is noticed that the grown crystals of salicylic acid admixtured TGS crystals crystallize in monoclinic structure. The space group and number of molecules per unit cell are found to be $P2_1$ and 2 respectively.

Table.2 Unit cell parameters of TGSS crystals

S. No.	Sample	Cell parameters	Volume of unit cell (Å)^3
1.	TGSS	a = 9.147(1) Å b = 12.742 3) Å c = 6.027(2) Å $\alpha = \gamma = 90^o$ $\beta = 105.27^o$ (2)	677.65

3.4 Spectral Studies by FTIR Technique

FTIR spectral studies are important in the investigation of molecular structure, examination of stretching, bending, twisting and vibrational modes of atoms in a molecule and hence to identify the functional groups of samples. The FTIR spectra were recorded for powdered samples of salicylic acid admixtured TGS using an FTIR spectrometer by KBr pellet technique. The recorded FTIR spectra of salicylic acid admixtured TGS crystals are shown in figure5. The observed vibrational wave numbers and their assignments for salicylic acid admixtured TGS crystals are tabulated in Tables 3. The IR spectral assignments for the bands/ peaks of FTIR spectra of the samples are given in accordance with the reported in the literature [18,19]. The broad band covering 3912 cm^{-1}- 3400 cm^{-1} region indicates the stretching frequencies of superimposed O-H and NH_3^+ modes. Multiple combination and overtone bands of CH_2 have been observed in the region 3002 cm^{-1} 2985 cm^{-1}. The absorption region 1700 cm^{-1} – 1650 cm^{-1} is assigned to C= O stretching of COOH group. Asymmetric bending vibrations and the absorption bands occurs at 500 cm^{-1} are due to symmetric NH_2 bending vibrations. The peaks around 700 cm^{-1} to 650 cm^{-1} assigned as SO_4^{2-} stretching vibrations lie in the same envelope of C-N stretch. The broadening or narrowing of some of the absorption bands / peaks of the FTIR patterns of the admixtured TGS crystals indicates that salicylic acid have entered into the host TGS crystals.

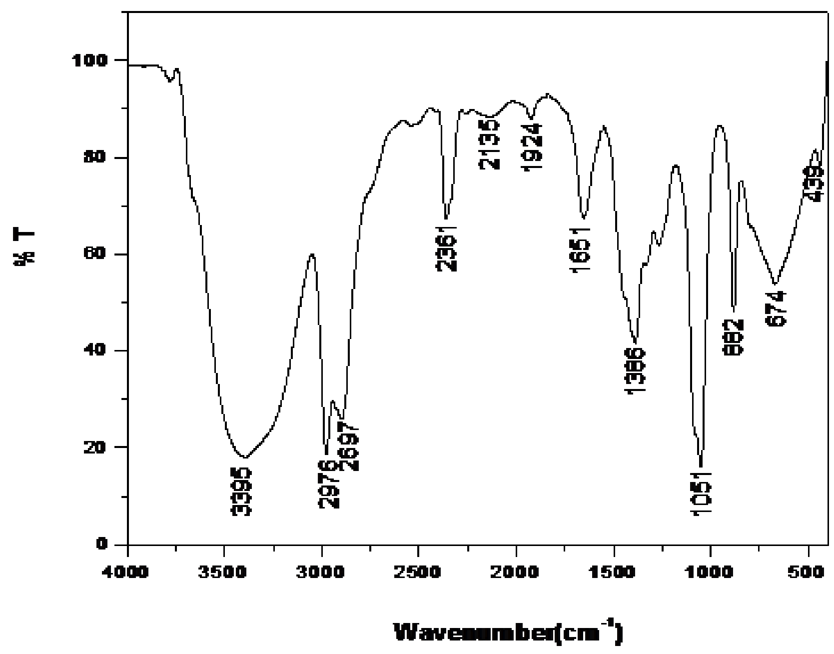

Figure5: FTIR spectrum of Triglycinesulpho salicylate (TGSS) single crystal

Table3: FTIR spectral assignments for TGSS crystals

Bands/Peaks (cm^{-1})	Assignments
3395	NH_3^+ asymmetric and OH stretching
2976	CH_2stretching
2697	C-Hstretchingmode
2361	StretchingofCH$_3$ vibration
2135	CombinationofNH$_3^+$ asymmetric stretching and torsional oscillation
1924	NH_3^+asymmetric bending
1651	Amide
1386	C–Cstretching
1051	OHbending
674	SO_4 Scissor bending
439	NH_3^+ torsion

3.5 Kurtz-Perry Technique (SHG)

Kurtz and Perry technique was used to check the NLO property of the samples [20]. The grown crystal of salicylic acid added TGSS are powdered and a high intensity Nd:YAG laser (λ=1064 nm) was used as source. The SHG was confirmed by the emission of green radiation (532 nm). The values of relative SHG efficiency of salicylic acid admixtured TGS crystals are found with reference to KDP. The obtained value of SHG efficiency is 1.11.Compared to that of pure TGS values the salicylic acid added TGS crystals have more SHG efficiency and hence these crystals are the potential candidates for NLOapplications.

3.6 Thermal Analysis

The TG/DTA thermal curves of TGSS crystal is shown in figure 6.The sample heated in a crucible between 30 °C and 1010 °C at a heating rate of 20 °C/minute in nitrogen atmosphere. The initial mass of the sample is 3.0540 mg at 30 ^{o}C but final mass left out after the experiment was only 0.06153% (0.0014154 mg) at 1000 ^{o}C (Figure 6) .The TG curve shows that there was weight loss of about 0.36 % in the temperature up to 113.33 ^{o}C. The maximum weight loss (53.41%) is observed in the temperature range 219.34 °C - 250.54°C. From DTA curve, it is observed that there is one endothermic peak at 244.47°C which represents the decomposition of TGSS sample. From this, it is concluded that the crystal decomposes only at 244.47 °C. The sharp endothermic peak shows good degree of crystallinity of the sample[21].

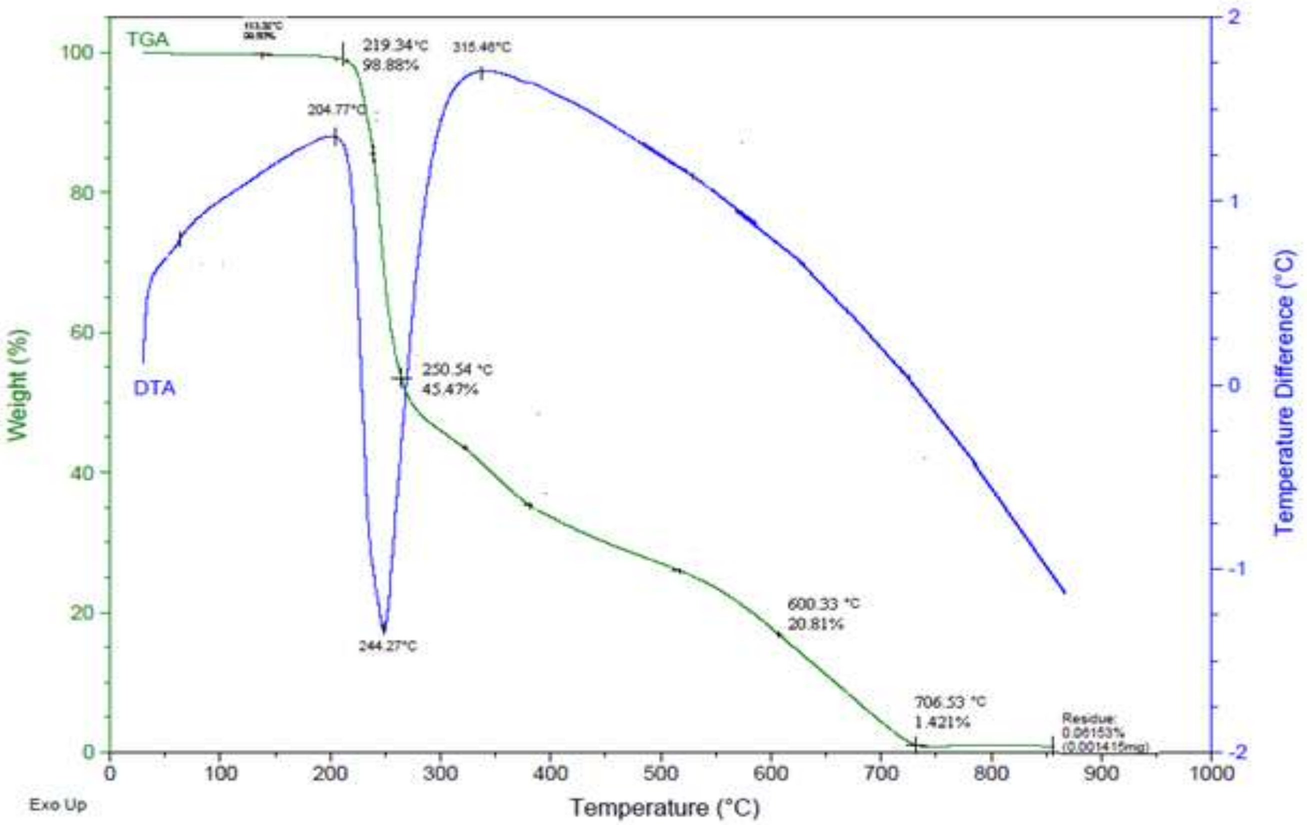

Figure6: TG/DTA Thermo grams of TGSS crystal

4. Conclusions:

Triglycine sulpho salicylate (TGSS) salt was synthesized and the solubility studies were carried out for various temperatures in the range 30-60^{o}C and it is observed that solubility increases with temperature. Metastable zone width and nucleation parameters were determined and using the optimized conditions, single crystals of TGSS were grown by slow evaporation technique. The grown crystals were subjected to XRD, spectral , thermal and SHG studies. The crystal structure of the grown TGSS crystal was found to be monoclinic structure.The powder SHG test confirms the NLO property of the sample crystals. From TG / DTA studies, the thermal stability of the grown crystals was confirmed. The functioned groups of the sample were obtained by the FTIR spectrum analysis.

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